The Kinetics of Decomposition of Acetylene in the 1500°K Region

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Introduction

The thermal decomposition of acetylene is one of the most-studied phenomena in the chemistry of gases. Despite the apparent simplicity of the C_2H_2 molecule, its thermal behavior is exceedingly complex. Within the past ten years, it has been studied in static systems (1, 2, 3), in flow systems (4-8), in shock tubes (9-12), and in flames (13). The temperature range covered in these studies has spanned the region from about 625°K to 2500°K, but with a gap in the 1000°K region that has been studied only very recently (6, 14). Explorations have been made of the product distributions, of the effects of vessel surfaces, of changing surface-to-volume ratios, of adding free radical capturers such as NO, and of adding organic compounds that might participate in the mechanism. The rate of formation and the characteristics of the carbons and polymers formed in the decomposition have been studied extensively.

There is substantial agreement on some aspects of the decomposition. It appears to be settled that at low temperatures, a homogeneous reaction which is second order in $[C_2H_2]$ dominates the behavior. The reaction is a chain and leads to the formation of high molecular weight compounds, with some side products such as H_2, C_2H_4, CH_4, and C_4H_4. The activation energy is approximately 50 kcal and the frequency factor of the uninhibited reaction is very large. Silcocks (3) gives

$$k = 3.72 \times 10^{16} \exp(-50.2 \text{ kcal}/RT) \text{ cc/mole sec.}$$

A heterogeneous reaction is also observed at low temperatures.

Silcocks reports that it is first-order in $[C_2H_2]$, with an activation energy of 42.7 kcal. He gives values of the rate constant at five temperatures.

The situation at high temperatures contains more conflict. It has been difficult to determine the order of the reaction and the activation energy, either with flow systems (8) or in shock tubes. However, if one presumes the reaction order to be integral, the best choice at high temperatures appears to be second-order in acetylene. The rate constants at the highest temperatures (9, 12) disagree by a factor of about 10, but agreement is considerably better at temperatures below 1900°K.

Both Aten and Greene (9) and Minkoff and Tipper (15) agree that the rate constants at high and low temperature can be used to define the rate over the whole range; i.e., they agree that the mechanism remains the same, at least up to and including the rate-determing step. However, Aten and Greene prefer their own high temperature data, while Minkoff and Tipper prefer those of Kistiakowsky and Bradley (12). These choices yield markedly different results, respectively:

$$\text{(data of ref. 9)}\ k = 10^{12.89} \exp(-39\ \text{kcal}/RT)\ \text{cc/mole sec}$$

$$\text{(data of ref. 12)}\ k = 10^{15.15} \exp(-45.8\ \text{kcal}/RT)\ \text{cc/mole sec}$$

Quite aside from questions raised by such a discrepancy, we think it unjustifiable to assume that one is measuring the rate of the same reaction sequence at 2000°K and at 700°K. The low temperature homogeneous reaction is a chain of length (3) on the order of 100 or more. There is no evidence that the reaction at high temperature is a chain. Indeed the only direct experimental evidence (12) of which we are aware indicates that it is essentially a simple sequence of consecutive reactions.

It is clearly important to discover what happens between the lower limit of the shock tube studies, ca. 1400°K, and the upper limit of the studies in vessels, ca. 800°K. This intermediate region is appropriate for studies using flow systems. Anderson and his colleagues (4, 5) have done exactly this, but have concentrated most of their attention upon product distributions and the implications of these regarding the mechanism. Very recently, however, Munson and Anderson (6) have published work from which it is possible to extract rate constant data and we shall discuss these later. Towell and Martin (8) used a flow reactor to study the decomposition over temperatures from about 1200°K to 1450°K. They had difficulty in defining the order of reaction, but their data compare reasonably well with shock tube data if one assumes second order behavior.

The present experiments represent an effort to study the decomposition very carefully at three temperatures, the highest of which overlaps the shock tube studies. Particular attention has been given to determining the order of reaction and the absolute magnitudes of rate constants at these three temperatures. The work is basically an extension of that performed by Kinney and Slysh (7).

Experimental Procedure

The apparatus was only slightly modified from the arrangement used by Kinney and Slysh (7) and will therefore be described only briefly. It was a flow system operating at ambient pressure. The pyrolysis tube was 5 mm i.d. refractory porcelain, sealed to Pyrex at the ends, and mounted in a furnace capable of attaining 1500°C. C_2H_2 was metered with a capillary flowmeter before being mixed with the helium carrier. Input rates were varied so as to produce mixture compositions ranging from 0.20 to 1.30 mole per cent C_2H_2.

Temperature profiles within the pyrolysis tube were measured with a Pt-Pt:Rh thermocouple for each of three temperature settings and at several flow rates. They were found to be essentially independent of flow velocity, from which it is inferred that the gas temperature was indeed being measured. This conclusion is supported by estimates of the radial temperature distribution in the tube based upon approximate values for the thermal diffusivity of the gas. The estimates show that the temperature at the center of the tube (2.5 mm from the wall) should not differ from the wall temperature by more than a few degrees. Because the furnace was short, the temperature profiles did not possess a plateau region. A typical profile is shown in Fig. 1, together with what we call the "staircase" approximation to it, by means of which it was possible to correct the experimental data to the temperature of an imaginary 5-cm-long hot zone having a constant temperature near the actual temperature peak. It was also convenient to discuss the effect of flow velocity upon the per cent decomposition in terms of the fictitious residence time ("contact time") of the gas in the imaginary hot zone.

Calculations of the extent of decomposition in the hot zone were carried out for each run by an iterative procedure in which an equation for the rate constant was assumed in order to compute the relative contributions from decomposition at each of the temperature levels on the staircase. Most of the decomposition occurred on the top level, which meant that it was quite easy to correct for the other contributions, using rough values for the rate constants in the first trial. From the results of the runs at three different temperature settings, a better expression for the temperature-dependent rate constant was derived and used in the second calculation of corrections. This single iteration was found to yield satisfactory values for rate constants at each of the three hot zone temperature levels (1333°K, 1433°K, and 1528°K). Details of these calculations are presented in reference 16.

The helium used was Matheson "research grade" gas, purity approximately 99.99%. It was passed through a bed of Cu at 400°C for O_2 removal and then through a tower containing Ascarite and Anhydrone to remove CO_2 and H_2O. The C_2H_2, a purified grade of 99.5% minimum purity, was bubbled through concentrated H_2SO_4 to remove acetone before introduction into the helium stream. The mixture of C_2H_2 and He was routed through a dry ice-cooled, glass wool-packed trap before entering a coil of tubing 4 feet in length that served to ensure homogeneity of the mixture that entered the pyrolysis tube.

Beyond the water-cooled exit of the furnace were three traps in series. The first was cooled by dry ice and served principally as a pre-cooler to ensure good trapping efficiency in the subsequent liquid N_2-cooled traps. These traps captured acetylene, diacetylene, vinylacetylene, methyl acetylene, and allene. Hydrogen and methane were not trapped, but were converted to H_2O and CO_2 over CuO filings at 700°C. Vitreous carbon that formed on the tube wall during the run was determined by burning it off with oxygen at 1255°C, running the effluent gas through a CuO trap, and capturing the CO_2 in Ascarite. A very small amount of reddish polymer, deposited just beyond the furnace exit, was the only product ignored. Analyses were performed using vapor chromatography and (for CO_2 and H_2O) by weighing Ascarite and Anhydrone absorption towers.

Results and Discussion

The decomposition has been studied at three temperatures: 1333°K, 1433°K, and 1528°K. These represent the effective hot zone temperatures to which the decomposition data were corrected. Because the emphasis in the present paper is upon the kinetics of decomposition, details of product analyses are not presented here. They were in broad agreement with the results of other investigations (6, 7). A note of special interest is that the more prominent C_4 product at 1333°K was vinylacetylene, but at 1528°K it was diacetylene.

In Table I are summarized the experimental data on the extent of decomposition of C_2H_2 at various nominal contact times. These formed the basis for calculations of rate constants. The order of reaction has been determined at the three hot zone temperatures by examining the extent of decomposition as a function of the initial concentration at fixed flow rate--i.e. at fixed effective contact time in the hot zone. The results appear in Fig. 2, and represent mixed first- and second-order behavior. This may be seen as follows: consider a reaction with rate given by

$$\frac{-dc}{dt} = k_u C + k_b C^2 \qquad (1)$$

Integration yields

$$\left(\frac{C_o}{C}\right) = k_u t + \int_o^t k_b C dt \qquad (2)$$

$$= (k_u + k_b \bar{C})t \qquad (3)$$

where $\bar{C}$ is a mean concentration over the time interval, and will approximately equal $(C_o + C)/2$ when the extent of decomposition is small. When this is the case, Eq. 3 yields

$$(1 - \frac{C}{C_o}) = (k_u + k_b\bar{C})t \qquad (4)$$

Thus for mixed first and second order, a study at fixed time (i.e. fixed flow rate) and small extent of decomposition should show an approximately linear dependence of the extent of decomposition upon the input concentration, with a finite intercept at $C_o = 0$ if there is in fact a first-order contribution. This is the case in Fig. 2.

One can calculate first-order rate constants from the intercepts in Fig. 1. The result for 1528°K is not as reliable as the other two because of the smaller number of points, the long extrapolation to $C_o = 0$, and the larger extent of decomposition. The calculations involve a correction to yield the extent of decomposition in the effective hot zone. This is in principle a multiply iterative procedure, but we found that the correction was sufficiently small that a rough treatment of the data could provide crude rate constants from which corrections could be formed to yield good rate constants in a single iteration, as discussed earlier.

The k_u values obtained are 0.221 sec^{-1} at 1333°K; 0.482 sec^{-1} at 1433°K; and 0.745 sec^{-1} at 1528°K. On an Arrhenius plot, these define a line given by

$$k_u = 4.2 \times 10^3 \exp(-26 \text{ kcal}/RT)\text{sec}^{-1}$$

The uncertainties in the numerical values of this expression are surely considerable (but difficult to estimate). Nevertheless it is clear that both the frequency factor and the activation energy rule out a homogeneous unimolecular reaction. If we assume that the reaction is heterogeneous, the rate constant k_{het} will be $k_{het} = k_u(V/S)$, where (V/S) is the volume-to-surface ratio. In our reactor, this ratio was 1.25×10^{-4} liter/cm^2, where the units have been chosen so as to permit easy comparison with the low-temperature results of Silcocks (3). The comparison is shown in Fig. 3. k_{het} is now given by

$$k_{het} = 5.25 \times 10^{-1} \exp(-26 \text{ kcal}/RT) \text{ liter cm}^{-2}\text{sec}^{-1}$$

An extension of this line goes through the middle of Silcocks' data. It is tempting to conclude that the heterogeneous reactions are the same, but caution is required because a modest alteration of the parameters in the expression for k_{het} could cause the extension to miss Silcocks' points altogether. There is much more to be explored on the matter of a heterogeneous decomposition. We have noted with interest that the yields of H_2, C_4H_4, and C_4H_2 all move toward zero at $C_o = 0$, and carbon plus CH_4 become virtually the only products. Clearly the mechanism of the surface decomposition must be grossly different from the gaseous process.

Fig. 2 shows that the gaseous decomposition conforms nicely to second-order kinetics, and it is possible to obtain k_b from the slopes. We have preferred to use data on the per cent decomposition as a function of the effective contact time in the hot zone, averaging the rate constants obtained from a number of runs (6 to 8) at the same temperature but at various flow rates and input concentrations. The results have been corrected, in each case, for the first-order contribution. The procedure (16) is tedious and will not be outlined here.

The results for k_b, in units of cc/mole sec, are: $(1.40 \pm 0.10) \times 10^3$ at 1333°K; $(3.42 \pm 0.23) \times 10^3$ at 1433°K; and $(2.49 \pm 0.36) \times 10^4$ at 1528°K. The uncertainties attached to each result are the average absolute deviations of the experimental points.

Figure 4 is an Arrhenius plot of all available data for k_b, ranging from about 650°K to 2500°K. The solid curve will be discussed later. Our data and those of Skinner and Sokolski (11) agree very well, in the sense that their higher-temperature points fall on the best line through our results. However, their values below about 1500°K (not included in the figure) show a change in slope that requires comment at a later point in this discussion. The data of Towell and Martin (8), obtained in reactors very similar to ours, parallel our data well. Agreement would be even better if their results could be readily corrected for the contribution from the heterogeneous decomposition. The results of Aten and Green (9) are in reasonable agreement with ours and with Skinner's but show a smaller slope. The best high temperature line, which we have selected by eye, defines k_b as

$$k_b = 3.2 \times 10^{14} \exp(-50 \text{ kcal}/RT) \text{ cc/mole sec.}$$

The frequency factor seems close to normal, in contrast to that cited earlier for the low-temperature reaction. This does not prove that one is observing an elementary reaction at high temperatures, but suggests that the hot reaction is not a chain. An extrapolation of the best high temperature line falls below the low temperature k_b values by a factor of 10^2 or more.

Thus the question remains: what happens between 800°K and 1400°K? The work of Munson and Anderson (6) contributes much toward an answer. They used a flow reactor of diameter 2.2 cm and, at high concentrations of C_2H_2 (20-21 mole per cent at $p_{tot} = 1$ atm), covered temperatures from 773°K to 1123°K. They did not obtain rate constants, but they do report the time-dependence of the C_2H_2 concentration at six temperatures. These results are of precision sufficient to permit examination of the reaction order by the usual methods of kinetics. Our analysis shows that the reaction is second-order in $[C_2H_2]$ at 873°K, 923°K, and 973°K, but that the order is not well defined at the higher temperatures. The second-order rate constants at the three lower temperatures are in remarkably good agreement with an extrapolation of low-temperature data.

If one approximates the kinetics at the three higher temperatures (1023°K, 1073°K, and 1123°K) by a first-order expression, the rate constants so obtained show a temperature coefficient corresponding to an activation energy in the vicinity of 30 kcal. It thus seems quite clear that the kinetics of the decomposition undergo a transition at about 1000°K, and that one cannot make a direct comparison of second-order rate constants at low and high temperatures.

In view of the known complexity of the decomposition, it is not really surprising to find complications in the kinetics; but the behavior does seem extraordinary. An acceptable mechanism must: (a) give second-order kinetics at low temperature, with a rate constant similar to that cited from the results of Silcocks; (b) there must be some sort of transition region at intermediate temperatures; and (c) at high temperatures the reaction must be second-order but now with k_b similar to that cited previously from our data and the shock tube data.

Behavior of this sort can occur in the mechanism presented below. This is offered as a stimulus to further work. It makes no attempt to account in detail for all products, and there is no direct evidence for the steps involved in it. Our comments follow each reaction postulated.

(1) $C_2H_2 + C_2H_2 \rightarrow C_2H_2{}^* + C_2H_2$.

This represents unimolecular excitation of acetylene to its lowest-lying triplet state. C_2H_2 is shown as the collision partner for the excitation on the presumption that in a mixture of C_2H_2 and a monatomic gas, e.g. He, C_2H_2 will be many times more effective than He because it can possess vibrational energy. The actual change of multiplicity probably occurs most rapidly when the amount of energy to be transferred is not very large (17). Thus a detailed mechanism for reaction 1 would include vibrational excitation. However, because establishment of vibrational equilibrium is probably rapid relative to the rate of reaction 1, one can think of at least one of the C_2H_2 molecules as being highly excited vibrationally without introducing a necessity for modifying the simple equation above.

Minkoff (2) has suggested that the first step is double excitation, $2\ C_2H_2 \rightarrow 2\ C_2H_2{}^*$. This has the virtue of being spin-allowed, but the energy requirement will be very much greater (roughly double) that for step 1 above; this should weigh more heavily against the double excitation than does the forbiddenness factor (perhaps 10^{-4}) entering into the rate constant of reaction 1.

Reaction 1 will probably have an energy barrier somewhat higher than the singlet-triplet excitation energy, which has been estimated (9) to lie between 42 and 67 kcal above the ground state, using data discussed by Laidler (17).

(2) $C_2H_2{}^* + C_2H_2 \rightarrow 2\ C_2H_2$,

deactivation of triplet acetylene. By microscopic reversibility, C_2H_2 must be much more effective than He in the deactivation. There will presumably be a small activation energy in the rate constant, and a forbiddenness effect in the pre-exponential factor.

(3) $C_2H_2^* + C_2H_2 \rightarrow C_4H_4^*$.

This is an addition reaction to yield a triplet dimer. The reaction will be in competition with step 2, and will be fast. The rate constant for a reaction that may be comparable, viz, the addition of NO_2 to C_2H_2, has been reported (18) to equal $10^{12.1}$ exp(-15 kcal/RT) cc/mole sec.

(4) $C_4H_4^* + C_2H_2 \rightarrow C_2H_2^* + C_4H_4$,

a chain-transfer reaction that is not simply an exchange of multiplicities because formation of vinylacetylene from $C_4H_4^*$ requires H atom migration. There should be an appreciable but small activation energy. We suspect that in a reaction of this type the collision efficiency ("steric" factor) may be very low.

(5) $C_4H_4^* + C_2H_2 \rightarrow$ products.

This alternative to reaction 4 is thought of as a radical addition reaction leading to stable products such as benzene. It is oversimplified for the sake of allowing a tractable expression for the overall kinetics. That is, it might also be thought of as a deactivation; or it might not end the chain at all, but rather continue it by a subsequent transfer reaction analogous to step 4; or the product might in turn add to C_2H_2. However, observations by Robertson et al. (19) of the yield of benzene in C_2H_2 pyrolysis do support the suggestion that a large fraction of the reaction events in step 5 do not lead to a continuation of the chain. It further appears from that work that reaction 5 has a large temperature coefficient. We shall assume that its activation energy is much larger than that for step 4, and that its collision factor is also much larger; in this way it becomes possible for its rate to be less than that of step 4 at low temperature but to exceed it at higher temperatures.

The postulated reaction scheme is terminated at this point. It is of course recognized in doing so that other reactions must occur. The scheme is a simplified version of that discussed by Minkoff and Tipper (15), but with the difference in the singlet-triplet excitation step noted previously.

A steady-state treatment of the scheme yields

$$-d\left[C_2H_2\right]/dt = \left[C_2H_2\right]^2 k_3(k_1/k_2)\left\{\left[3 - k_4/(k_4 + k_5)\right]/\left[1 + (k_3/k_2)k_5/(k_4 + k_5)\right]\right\} \qquad (4)$$

At low temperatures, we expect $k_4 >>> k_5$. Then

$$-d\left[C_2H_2\right]/dt \doteq 2\left[C_2H_2\right]^2 k_3(k_1/k_2)\left[1/(1 + k_3k_5/k_2k_4)\right] . \qquad (5)$$

We expect k_3 to be considerably greater than k_2; but with $k_4 >>> k_5$, the result is

$$-d\left[C_2H_2\right]/dt = 2\left[C_2H_2\right]^2 k_3(k_1/k_2) \qquad (6)$$

At higher temperatures, k_5 will compete with k_4 and the chain length will be reduced. In the limit that $k_5 >> k_4$, continuing to assume $k_3 >> k_2$, the steady-state treatment yields

$$-d[C_2H_2]/dt = 3k_1[C_2H_2]^2 \ . \qquad (7)$$

This rate will be substantially less than that given by the previous result, if extended to high temperature. The consequence is that at the temperature where k_5 begins to compete effectively with k_4, an Arrhenius plot of the apparent second-order rate constant should begin to show a decreasing slope. Once the condition, $k_5 >> k_4$, is reached, the slope will rise again to that characteristic of k_1. This seems to conform rather well to the plot in Fig. 4. The transition region for k_4 versus k_5 appears to begin at about 900°K and extends to about 1400°K.

The high-temperature results cited earlier now yield

$$k_1 = 1.1 \times 10^{14} \exp(-50 \text{ kcal}/RT) \text{ cc/mole sec}$$

and, using this k_1, the low-temperature results of Silcocks yield

$$(k_3/k_2) = 1.60 \times 10^2 \ .$$

If we require that $(k_4/k_5) = 10(k_3/k_2)$ at 700°K and $(k_4/k_5) = 0.2$ (i.e. << 1) at 1400°K, the temperature dependence of (k_5/k_4) is found to be

$$(k_5/k_4) = 4.2 \times 10^4 \exp(-25.1 \text{ kcal}/RT) \ .$$

Employing these three parameters, k_1, (k_3/k_2), and (k_5/k_4), Equation 4 may be used for a computation of the second-order rate constant over the whole temperature range. The result is shown by the solid curve in Fig. 4. The fit seems quite successful, particularly when it is realized that the C_2H_2 disappearance rates reported by Munson and Anderson may have been appreciably enhanced by heterogeneous decomposition on carbon particles formed in their reactant stream. It is not possible to make a correction for this effect; the point is that the k_b values computed from their results are probably too large.

Some comment on the parameters is in order. k_1 has a surprisingly large pre-exponential factor, in view of the violation of spin conservation in reaction 1. However, in a recent study of SO_2 decomposition, Gaydon et al. (20) have found that unimolecular excitation of SO_2 to its lowest triplet state appears to be aided by energy transfer from internal degrees of freedom. This has the effect of raising the pre-exponential factor so as to largely compensate for the forbiddenness of the reaction. The apparent energy of activation is lowered in such a case. In C_2H_2-C_2H_2 collisions, there are many possibilities for energy transfer from internal modes and it is possible to rationalize k_1 on this basis. If the interpretation is correct, then the true activation energy of step 1 probably lies between 55 and 60 kcal, and a simple Arrhenius expression for k_1 is not very realistic. However, refinement of k_1 does not yet seem justifiable.

The (approximate) temperature independence of (k_3/k_2) is about what one would expect on the basis of the earlier discussion of these reactions. The magnitude of the ratio, i.e. 160, is also reasonable.

As for (k_5/k_4), the large ratio of pre-exponential factors is not unexpected, but no particular significance can be attached to the 25 kcal difference in activation energies except to say that it seems consistent with the experimental results of Robertson et al. (19). Beyond this, our ignorance of the details of the postulated steps 4 and 5 is almost total.

A final remark should be made on the report by Skinner and Sokoloski (11) that the rate constant for formation of vinylacetylene below about 1500°K lies above the low-temperature extension of their results for conversion to all products at temperatures above 1500°K (points shown in Fig. 4). If the result is real, it presents a severe complication. We would suggest tentatively that their low yields of vinylacetylene may have led to analytical errors, as indicated to some extent by their difficulty in obtaining a mass balance on reactants plus products.

Conclusions

It is possible to reconcile most low- and high-temperature data in the literature on acetylene pyrolysis by a chain mechanism in which the main chain-ending reaction has a stronger temperature dependence than does one of the chain-carrying reactions. This leads to long chains at low temperatures and essentially non-chain behavior at high temperatures. It seems very probable that the first step in the mechanism is excitation of C_2H_2 to its lowest-lying triplet state, and that one of the chain steps is a spin-exchange reaction.

In systems possessing high surface-to-volume ratios, e.g. in heavily sooting systems, a first-order heterogeneous decomposition reaction, the products of which appear to be principally carbon and CH_4, is expected to dominate the kinetics.

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References

1. G. J. Minkoff, D. M. Newitt, and P. Rutledge, J. Appl. Chem. **1957**, 406.
2. G. J. Minkoff, Can. J. Chem. **36**, 131 (1958).
3. C. G. Silcocks, Proc. Roy. Soc. **A242**, 411 (1957).
4. F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Sixth Symposium (International) on Combustion*, New York, Reinhold (1957), p. 247.
5. F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Eighth Symposium (International) on Combustion*, Baltimore, Williams and Wilkins (1960), p. 775.
6. M. S. B. Munson and R. C. Anderson, Carbon **1**, 51 (1963).
7. C. R. Kinney and R. S. Slysh, *Proceedings of the Fourth Carbon Conference*, Oxford, Pergamon Press (1960), p. 301.
8. G. D. Towell and J. J. Martin, A.I.Ch.E. Jour. **7**, 693 (1961).
9. C. F. Aten and E. F. Greene, Combustion and Flowe **5**, 55 (1961).
10. W. J. Hooker, *Seventh Symposium (International) on Combustion*, London, Butterworths (1959), p. 949.
11. G. B. Skinner and E. M. Sokoloski, J. Phys. Chem. **64**, 1952 (1960).
12. J. N. Bradley and G. B. Kistiakowsky, J. Chem. Phys. **35**, 264 (1961).
13. J. D. Chase and F. J. Weinberg, Proc. Roy. Soc. **A275**, 411 (1963).
14. C. F. Cullis, Dept. of Chemical Engineering and Chemical Technology, Imperial College, London; private communication of work in press.
15. G. J. Minkoff and C. F. H. Tipper, *Chemistry of Combustion Reactions*, London, Butterworths (1962).
16. F. L. Dormish, M. S. Thesis, Dept. of Fuel Technology, The Pennsylvania State University, University Park, Pa., 1962.
17. K. J. Laidler, The Chemical Kinetics of Excited States, Oxford, 1955.
18. J. H. Thomas, Trans. Faraday Soc. **48**, 1142 (1952).
19. W. W. Robertson, E. M. Magee, J. Fain, and F. A. Matson, *Fifth Symposium (International) on Combustion*, New York, Reinhold (1955), p. 628.
20. A. G. Gaydon, G. H. Kimbell, and H. B. Palmer, Proc. Roy. Soc. **A276**, 461 (1963).

Table I.

Summary of experimental data on the decomposition rate

1333°K#			1433°K#			1528°K#		
c.t.* (sec)	C_o (mole %)	% Dec.	c.t.* (sec)	C_o (mole %)	% Dec.	c.t.* (sec)	C_o (mole %)	% Dec.
0.100	0.58	3.9	0.100	0.50	8.2	0.046	0.50	9.1
0.150	0.57	5.6	0.150	0.22	11.2	0.094	0.50	18.2
0.150	0.81	6.3	0.150	0.27	11.4	0.150	0.50	31.2
0.150	0.96	6.5	0.150	0.52	12.8	0.150	0.69	37.7
0.150	1.02	7.2	0.150	0.97	14.3	0.150	0.78	39.7
0.150	1.28	7.5	0.150	1.25	16.5	0.180	0.50	37.0
0.200	0.52	7.5	0.150	1.30	16.8	0.190	0.50	37.8
			0.200	0.53	18.1			

# Hot zone temperature.

* Nominal contact time = (hot zone volume)/(vol. flow rate at hot zone temperature).

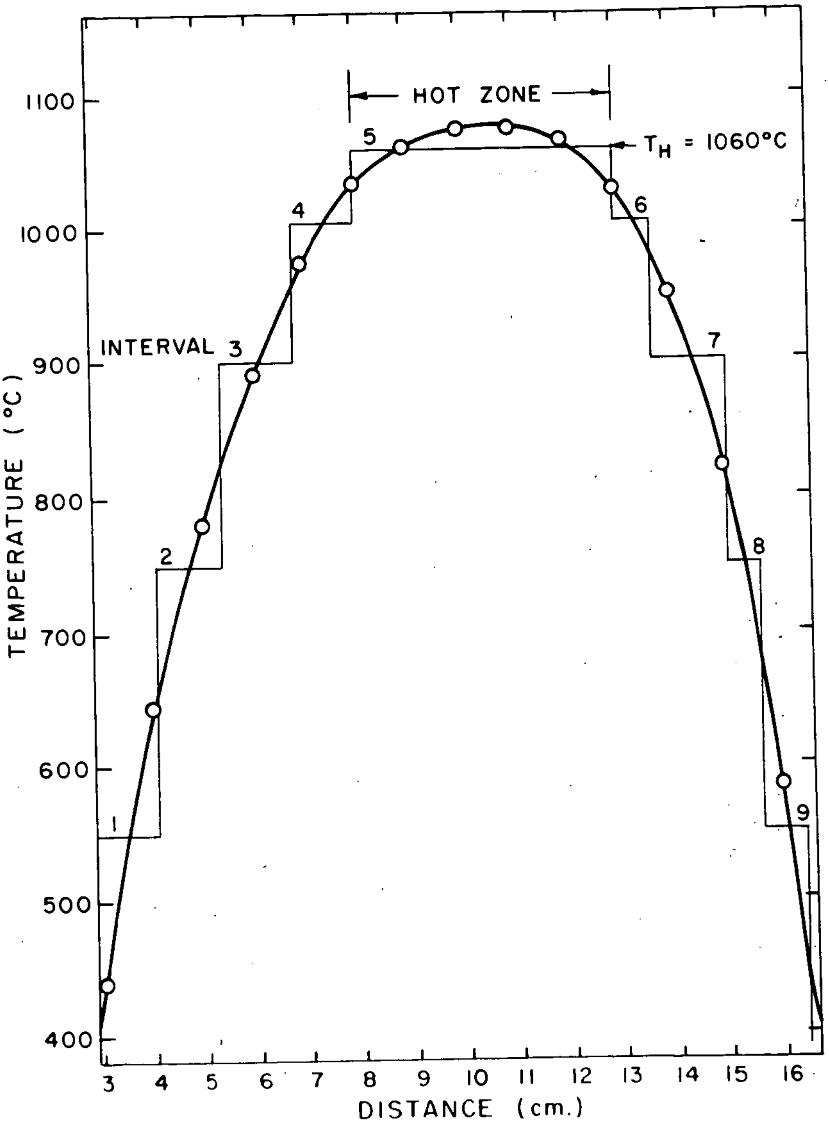

Fig. 1. Temperature profile for the furnace having the hot zone at 1060°C (1333°K). The "staircase" approximation to the profile is illustrated.

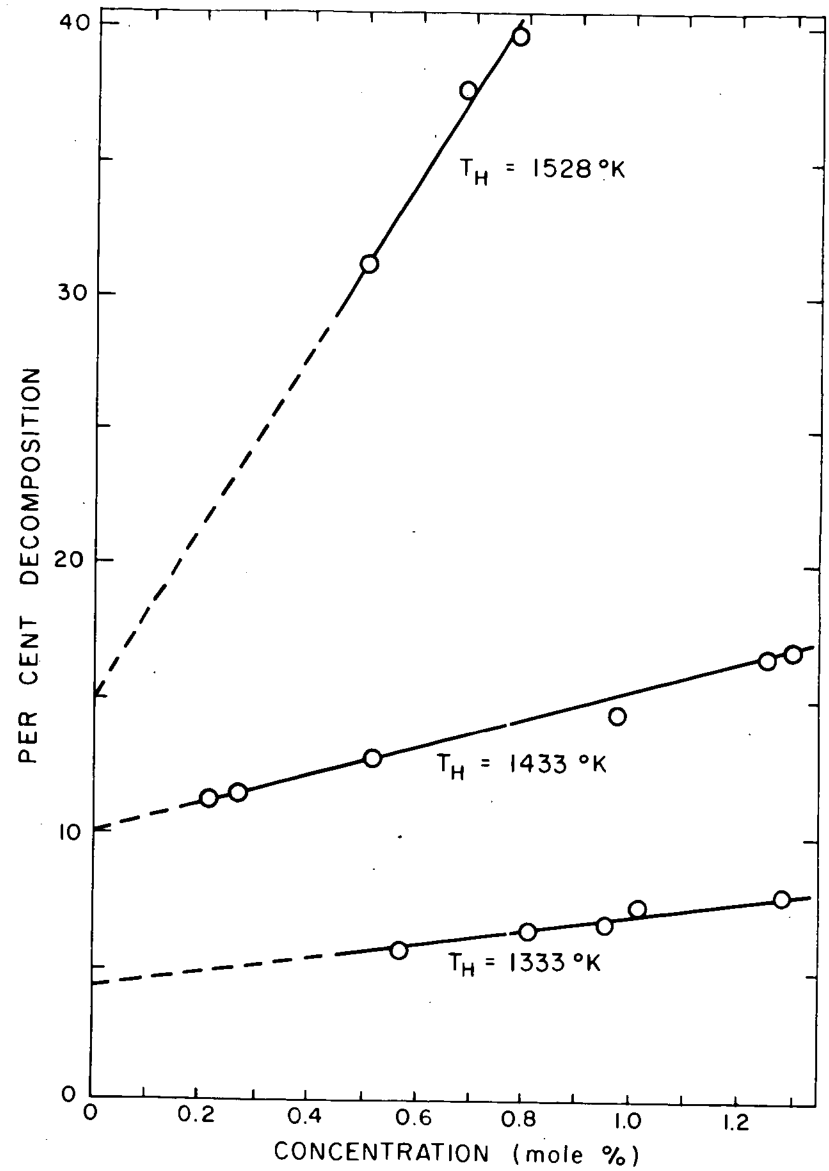

Fig. 2. Effect of change in initial concentration upon extent of decomposition at fixed contact time (0.150 sec).

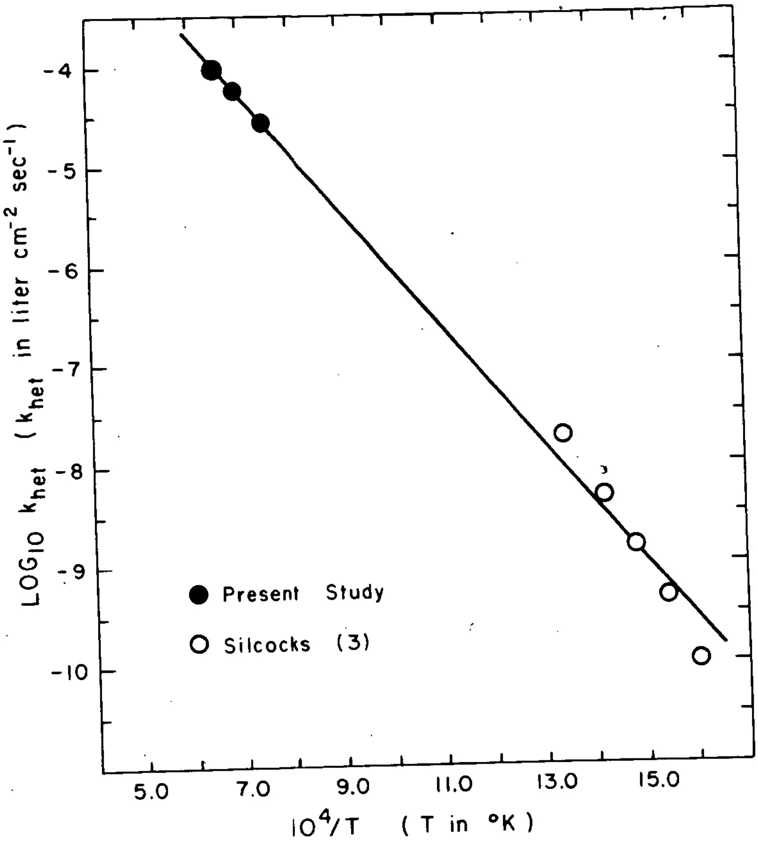

Fig. 3. Arrhenius plot of heterogeneous rate constants for C_2H_2 decomposition from the present work and from Silcocks (3).

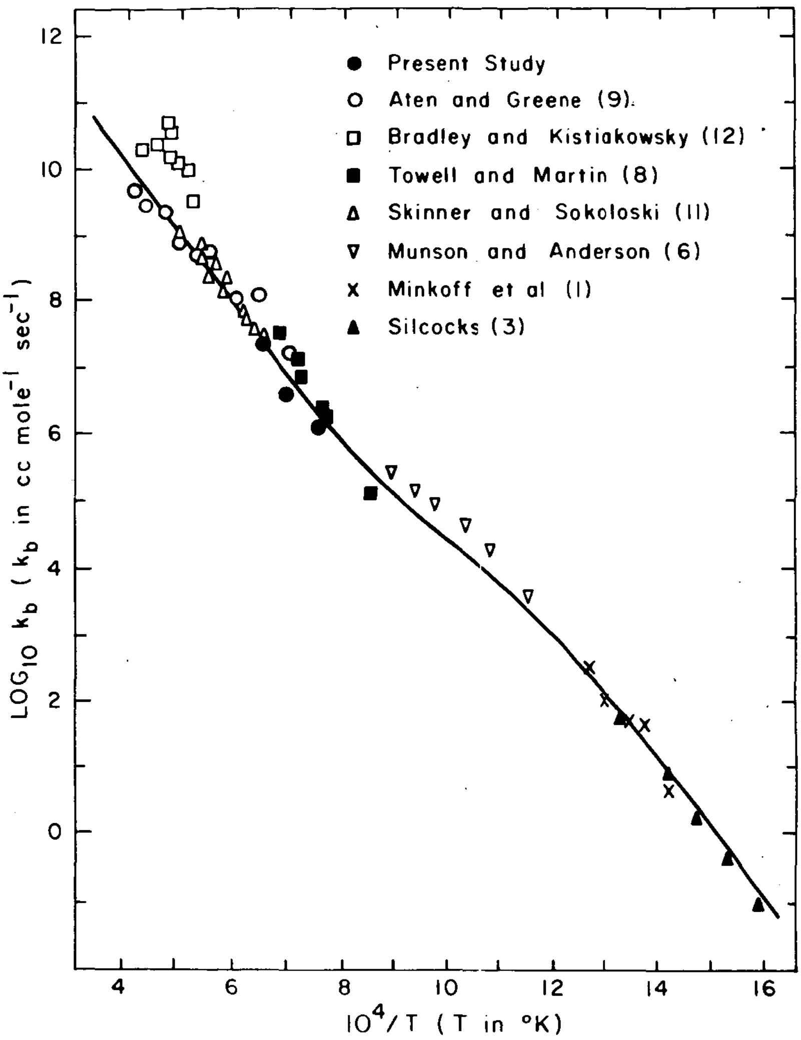

Fig. 4. Arrhenius plot of second-order rate constants for acetylene decomposition from the present work and from the literature.